UNIVERSITA' DI MESSINA
FACOLTA' DI SCIENZE

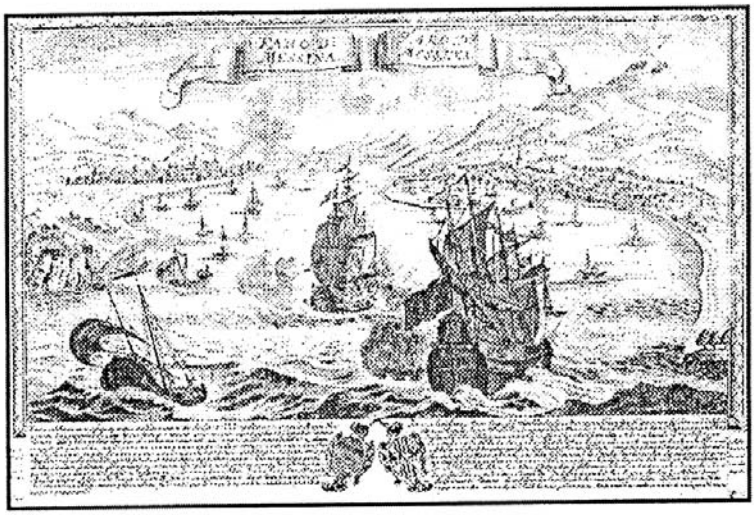
Dipartimento di Chimica Inorganica, Analititca
e Struttura Molecolare

Società Chimica Italiana
visione di Chimica Inorganica

Atti Accademia Peloritana dei Pericolanti
Classe I di Scienze Fisiche
Matematiche e Naturali

WORKSHOP ON PLATINUM CHEMISTRY

ABSTRACTS



MESSINA 30-31 MAGGIO 1994
Aula dell'Accademia

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Classe I di Scienze Fis. Mat. e Nat.
Vol. LXXII (1994) - Convegno 30-31 maggio 1994

HETEROMETALLIC PLATINUM CARBONYL CLUSTERS: SYNTHETIC STRATEGIES AND MOLECULAR GEOMETRIES

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Heterometallic carbonyl clusters are helpful models for the metallic state and for the stereochemical implications concerning the chemi- and physisorption of carbon monoxide into metal surfaces. [1] However, a prerogative of a molecular metal cluster, strictly related to the presence of ligands, is the possibility of adopting different metal packings, no matter what metal packing is adopted in bulk, and, at the same time, of showing unusual structure forbidden in bulk. Thus, the occurrence of a particular metal polyhedron in heterometallic carbonyl clusters is probably due to a delicate balance between electronic needs of different metals, internal and external steric factors and crystal lattice requirements.

The present lecture will focus mainly on high-nuclearity carbonyl metal clusters containing platinum, an electron-rich metal with a relatively high atomisation energy, which is able to support and stabilize large metal skeletons with relatively few carbon monoxide ligands. As a matter of fact, due to the progressive flattening of the polyhedral surfaces, the steric

requirements of the ligands increase exponentially with the cluster size.[2]

In this lecture, the synthetic strategies (thermal activation, oxidative condensation or coupling, reductive carbonylation and redox condensation, etc.) and the molecular geometries (polyhedra as bulk metal fragments, condensed polyhedra, etc.) of the more significant high-nuclearity heterometallic platinum carbonyl clusters will be systematically presented by giving an overview of the already known $Pt-Rh$, $Pt-Ni$ and $Pt-Os$ systems [3] and presenting more recent results on the synthesis and characterization of new large carbonyl metal clusters belonging to the $Pt-Ru$ system, viz. $[Ru_9Pt_6(CO)_{28}]^{4-}$ and $[Ru_6Pt_3H_2(CO)_{21}]^{2-}$. The molecular structures of the above $Pt-Ru$ anionic clusters are nice examples of polyhedra as bulk metal fragments (b.c.c.), as in $[Ru_9Pt_6(CO)_{28}]^{4-}$ and of condensed polyhedra (face sharing octahedra), as in $[Ru_6Pt_3H_2(CO)_{21}]^{2-}$. Very recent results on the $Pt-Sn$ system will be also presented and discussed. Such a system is extremely important for its potential implication in the catalytic hydroformylation. The $[Pt_8(SnCl_2)_4(CO)_{10}]^{2-}$ and $[Pt_6(SnCl_2)_2(SnCl_3)_4(CO)_6]^{4-}$ anionic clusters have been prepared by reacting a Pt carbonyl cluster, belonging to the series of inorganic oligomers $[Pt_3(CO)_6]_n^{2-}$ $(n=3,4,5)$, with $SnCl_2$. The purpose of this chemistry was to cheek the behaviour of a molecular metal cluster with an electrophile and to test whether the site of interaction could be the softer part of the cluster, e.g. the metal core, or the harder part represented by the oxygen atoms of the carbonyl groups. The above $Pt-Sn$ anions have been completely characterized by x-ray analysis. The molecular structure of $[Pt_8(SnCl_2)_4(CO)_{10}]^{2-}$ can be described as a cluster-adduct deriving from the condensation of three edge-sharing tetrahedra of Pt atoms bearing intact $SnCl_2$ into external "butterfly"surfaces. Instead, in the $[Pt_6(SnCl_2)_2(SnCl_3)_4(CO)_6]^{4-}$ anionic cluster

two edge-sharing tetrahedra of Pt atoms, forming the metallic skeleton, bear two $SnCl_2$ moieties and four additional $SnCl_3^-$ groups as edge- face-bridging ligands.

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